



Ultrafast Structural Dynamics in Solvated Transition-metal Complexes and Oxide Materials

R.W. Schoenlein

*Materials Sciences Division
Chemical Sciences Division - UXSL*



**Advanced Photon Source 'SPX' Workshop
May 9, 2007**

LAWRENCE BERKELEY NATIONAL LABORATORY

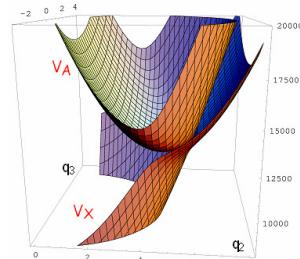
Fundamental Challenge – Condensed Matter

Understand the Interplay between Atomic and Electronic Structure

- Valence electronic structure – energy levels, charge distribution, bonding, spin
- Atomic structure – coordination, atomic arrangements, bond distances

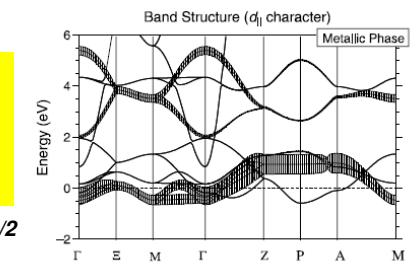
Particularly in systems that challenge the standard paradigms :

- beyond single-electron band structure models, Landau-Fermi Liquid Theory complex materials exhibiting strong correlation among charges, and between charge, spin, orbit, and lattice



*- beyond simple adiabatic potential energy surfaces
Born-Oppenheimer approximation*

$$\Psi_{\text{total}} \neq \Psi_{\text{nuclear}} \Psi_{\text{electronic}}$$



$$T_{\text{lifetime}} \neq (E - E_F)^{-1/2}$$

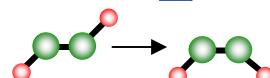
Atomic Structural Dynamics

atomic vibrational period: $T_{\text{vib}} = 2\pi(k/m)^{-1/2} \sim 100 \text{ fs}$
 $k \sim \text{eV}/\text{a}^2 \quad m \sim 10^{-25} \text{ Kg}$

- structural phase transitions



- chemical reactions



Electronic Structural Dynamics

electron-phonon interaction $\sim 1 \text{ ps}$
e-e scattering $\sim 10 \text{ fs}$
e- correlation time $\sim 100 \text{ attoseconds (a/V}_{\text{Fermi}}\text{)}$

- bond dynamics, valence charge flow
- electronic phase transitions
- correlated electron systems

Ultrafast X-rays: Quantitative Information on Electronic and Atomic Structure



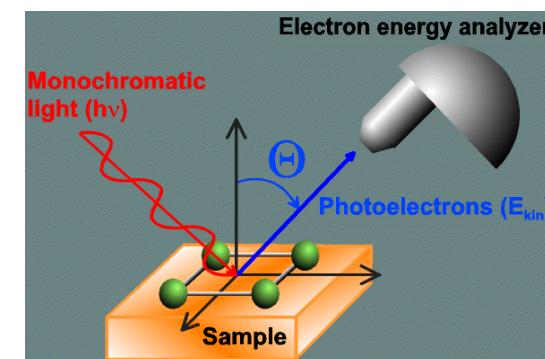
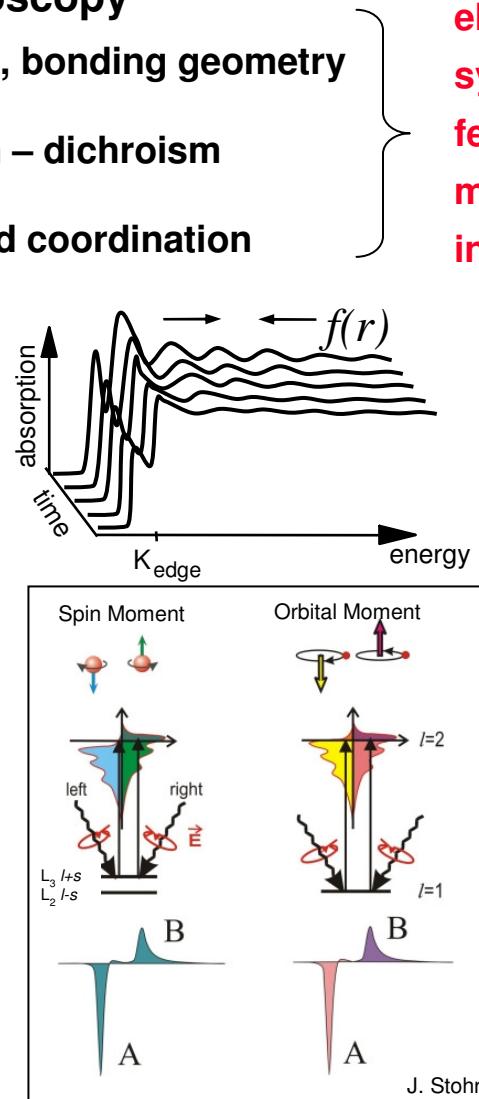
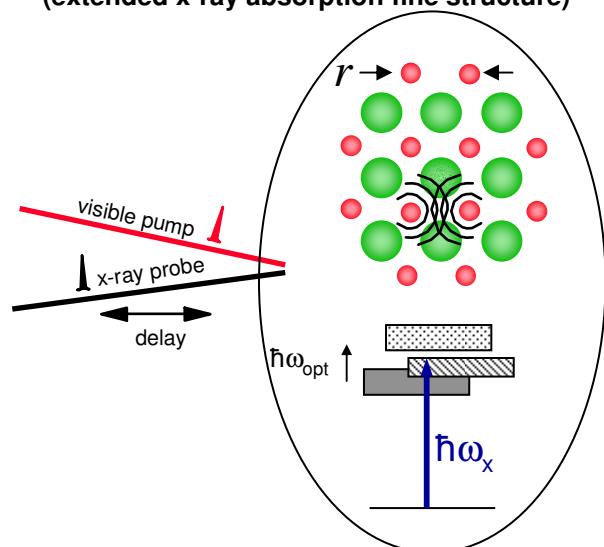
time-resolved x-ray spectroscopy

XANES – local electronic structure, bonding geometry
(x-ray absorption near-edge structure)

XMCD, XMLD – spin,magnetization – dichroism
(x-ray magnetic/linear dichroism)

EXAFS – local atomic structure and coordination
(extended x-ray absorption fine structure)

element specific
symmetry/spin selective
ferromagnetic/antiferromagnetic order
molecular systems and reactions
interfaces, complex/disordered materials

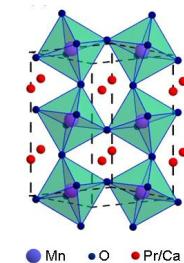


Photoemission – occupied states
single particle spectral density fcn. $\mathbf{A}(\mathbf{k}, \omega)$
X-ray Absorption – unoccupied states

Outline

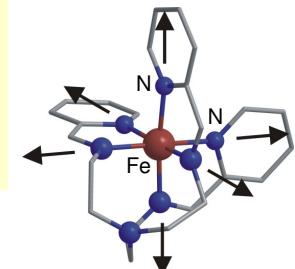
Structural Dynamics in Colossal Magnetoresistive (CMR) Manganites

- ultrafast photo- and vibrationally-induced insulator-metal transition in $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$
- electronic structure – time-resolved XANES (O K-edge, Mn L-edge)



Structural Dynamics in Solvated Transition-Metal Complexes

- spin-crossover transition – Fe(II) complex – EXAFS, Fe K-edge (atomic structure)
- spin-crossover – Fe(II) – XANES, Fe L-edge (electronic structure)



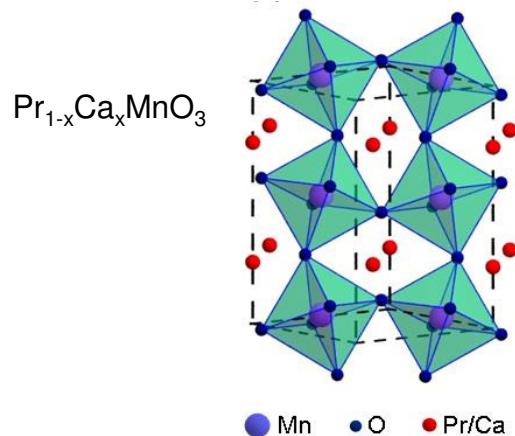
Ultrafast X-ray Science Facility at the Advanced Light Source

- development undulator based beamlines for femtosecond x-rays

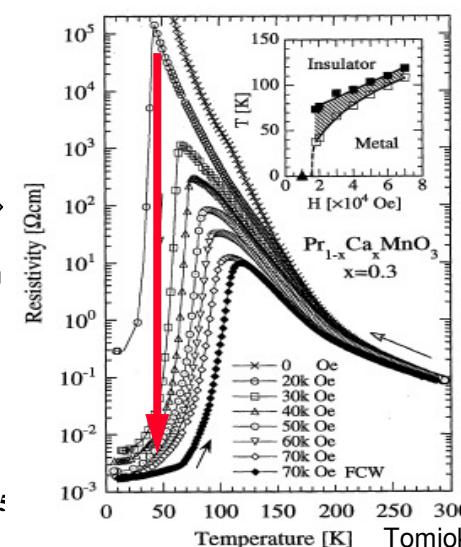
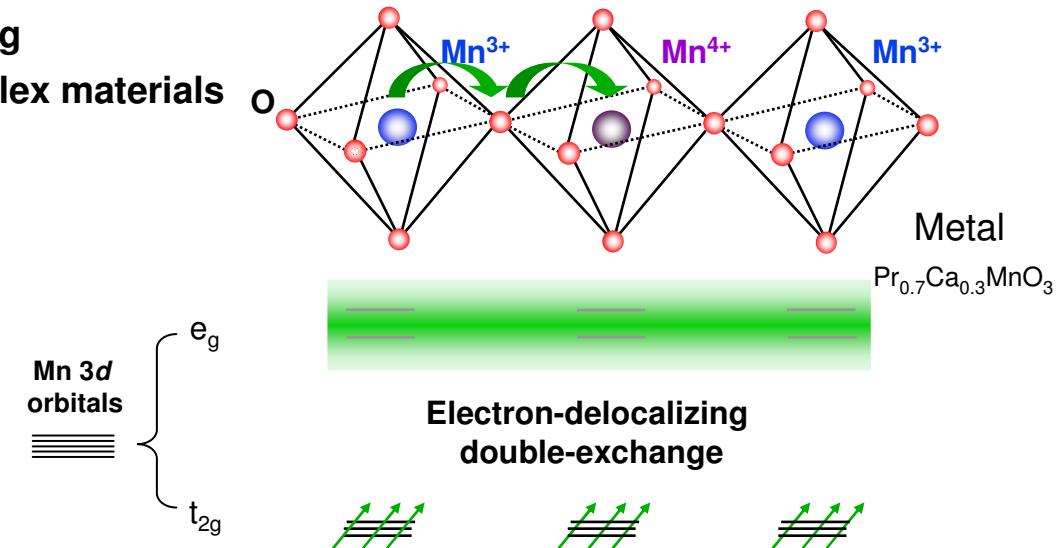
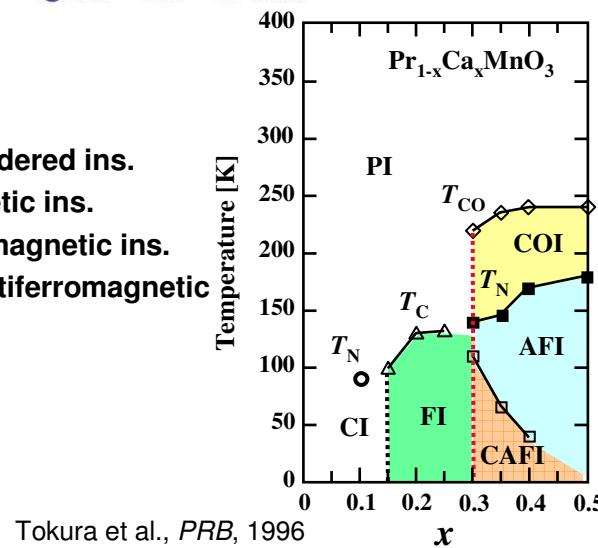
Colossal Magnetoresistive Manganites



- magnetic control of electronic structure (magneto-transport)
- rich phase diagram – order/symmetry breaking
- new physics, correlation effects – other complex materials



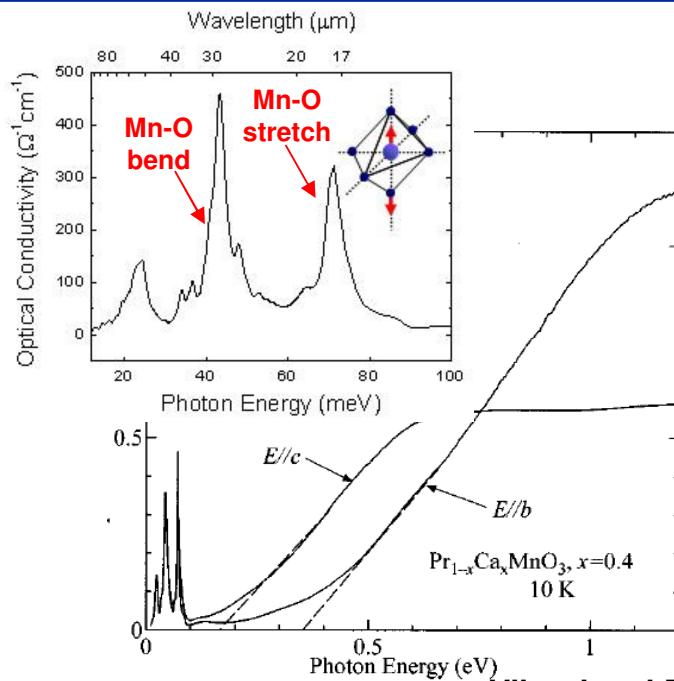
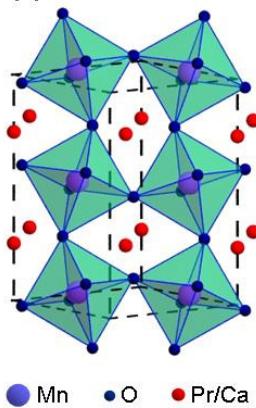
COI - charge ordered ins.
 PI – paramagnetic ins.
 AFI – antiferromagnetic ins.
 CA – canted antiferromagnetic



I-M Phase Transition Induced by:

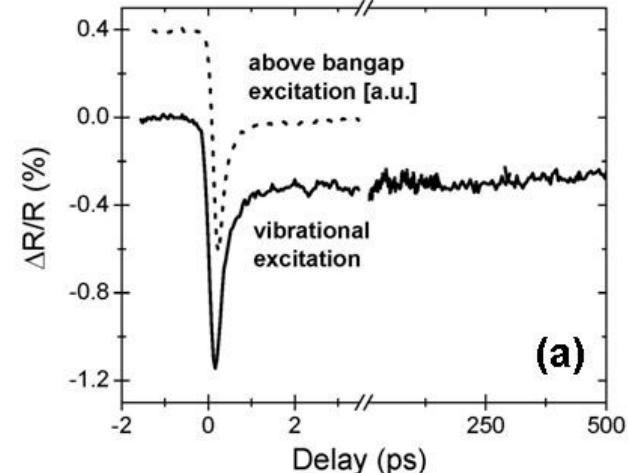
- applied magnetic field (CMR)
 - pressure
 - **ultrafast optical excitation**
 - **coherent vib. excitation**
 - Mn-O stretch
 - practical applications
 - fundamental physics
 - atomic/electronic
 - structural dynamics
- ~200 fs**

Vibrationally Driven I-M Transition in a Manganite via coherent THz excitation

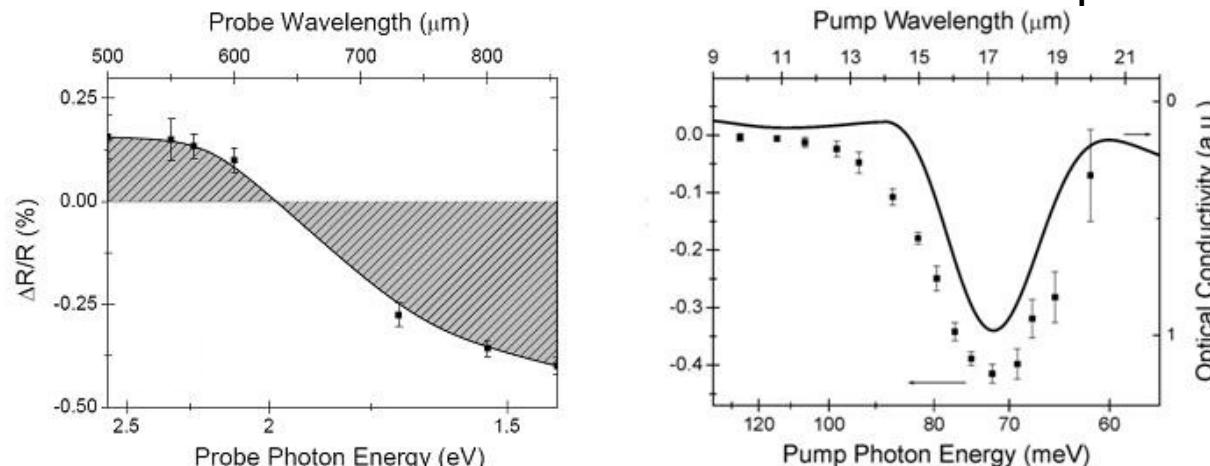


M. Rini, et al., *Nature*, 2007

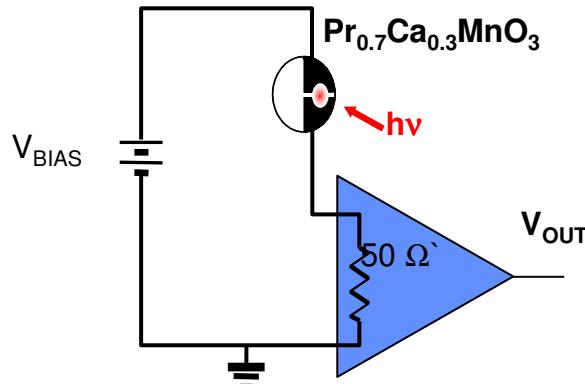
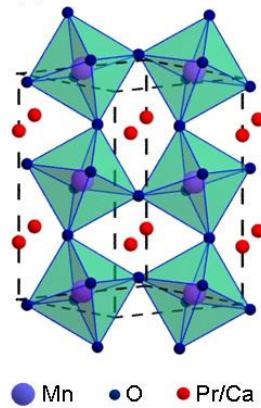
Transient Reflectivity



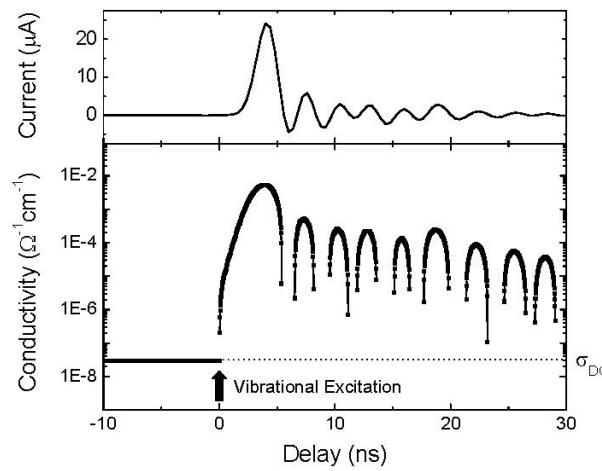
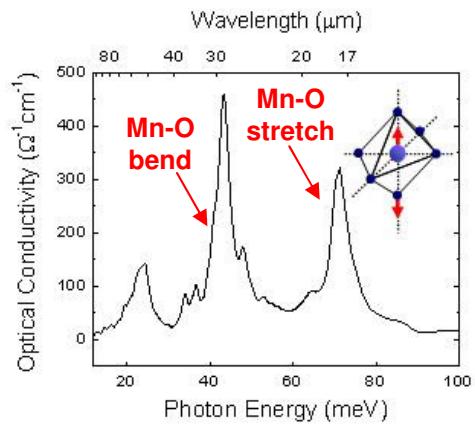
Vibrational Resonance Dependence



Vibrationally Driven I-M Transition in a Manganite via coherent THz excitation

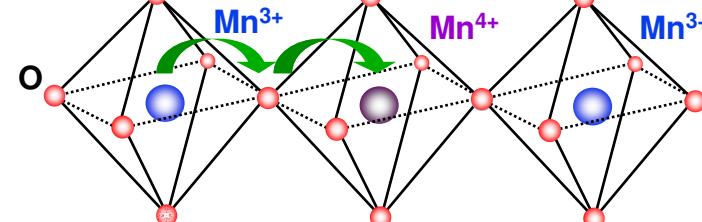
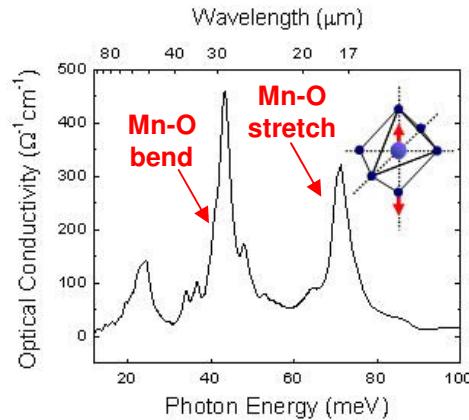


Direct Measure of Transient Conductivity



M. Rini, et al., *Nature*, 2007

Vibrationally Driven I-M Transition in a Manganite via coherent THz excitation

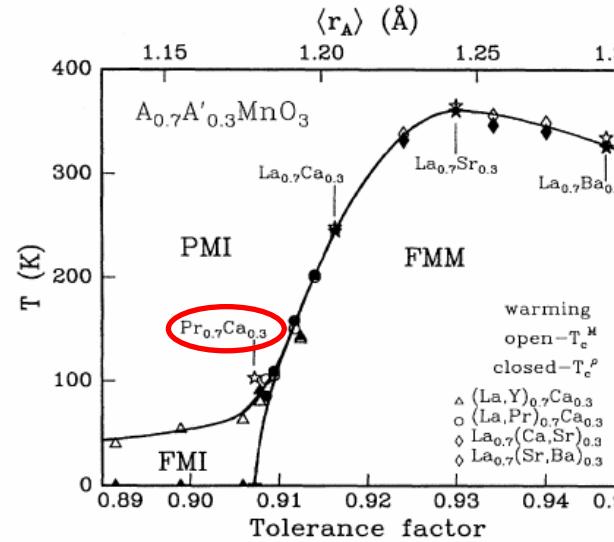


small tolerance factor \leftrightarrow charge localization

Tolerance Factor

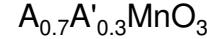
$$\Gamma = \frac{d_{A-O}}{\sqrt{2} \cdot d_{Mn-O}}$$

e^- hopping rate

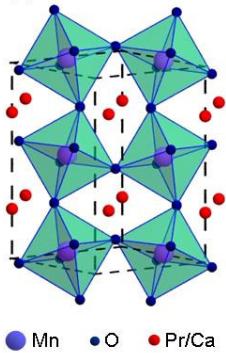


Hwang et al.,
PRL, 75 (1995)

Generalized Phase Diagram

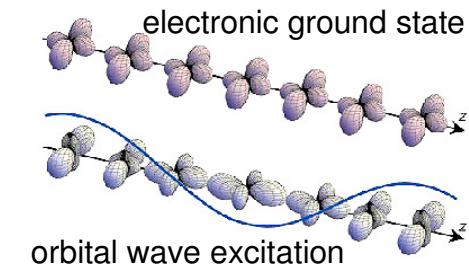


Ultrafast X-rays - New Insight on Complex Materials



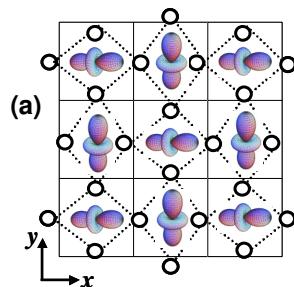
Vibrationally Driven I-M Transition in a Manganite

- THz vibrational control of correlated-electron phases targeting specific vibrational modes - Mn-O stretch
- Ultrafast I-M phase transition - electronic ground state $\times 10^4$ resistivity change



Future Scientific Questions and Challenges:

Crystallographic distortion associated with electronic phase transitions?
ultrafast x-ray diffraction, EXAFS



Magnetic nature of the metallic phase – ferromagnetic?
ultrafast x-ray dichroism

Dynamics of electronic structure - charge/orbital ordering?
*ultrafast resonant x-ray diffraction
time-resolved soft x-ray microscopy (phase separation)*

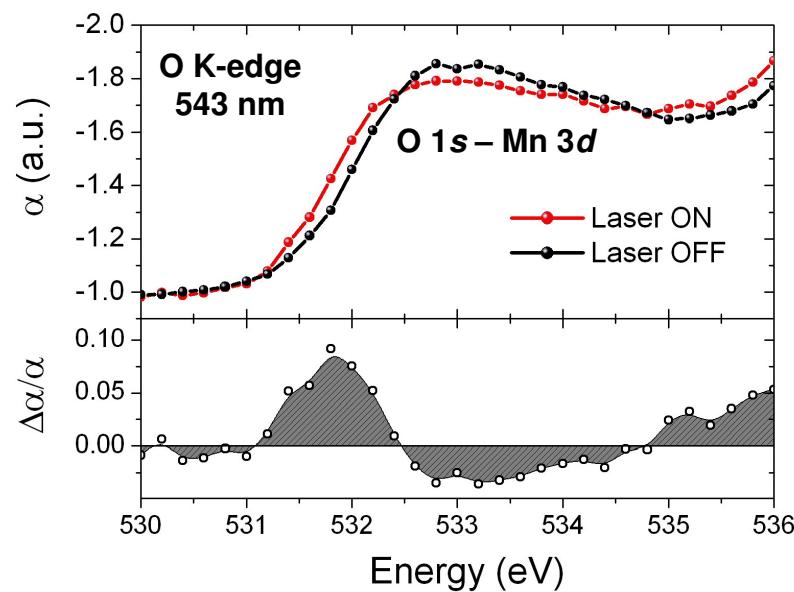
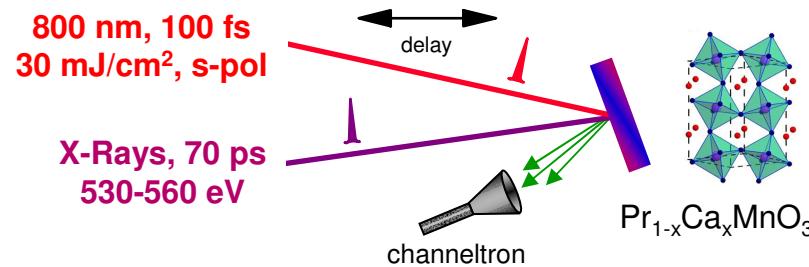
Dynamics of electronic structure – charge localization/delocalization?
*ultrafast XAS – 3d-2p hybridization
ARPES – dynamic band structure, valence charge distribution*

Ultrafast x-ray techniques relevant for a broad range of complex materials
(organics, multiferroics, novel superconductors.....)

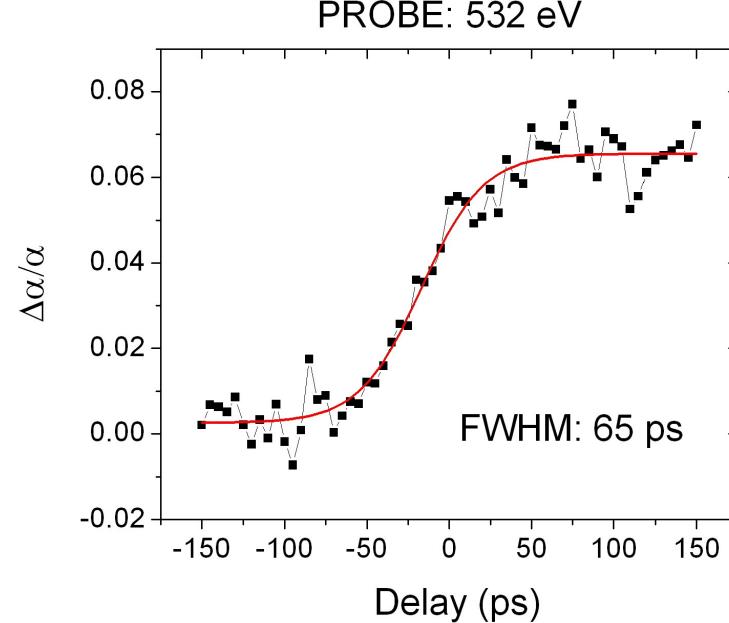
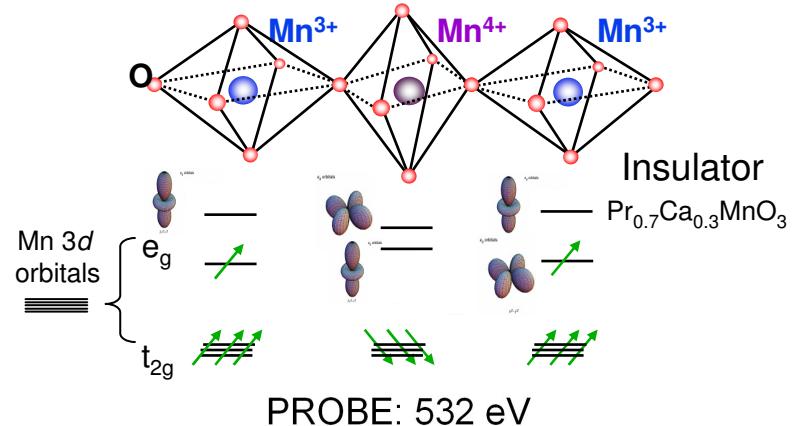
Time-resolved XAS Insulator/Metal Transition in Manganite (PCMO)



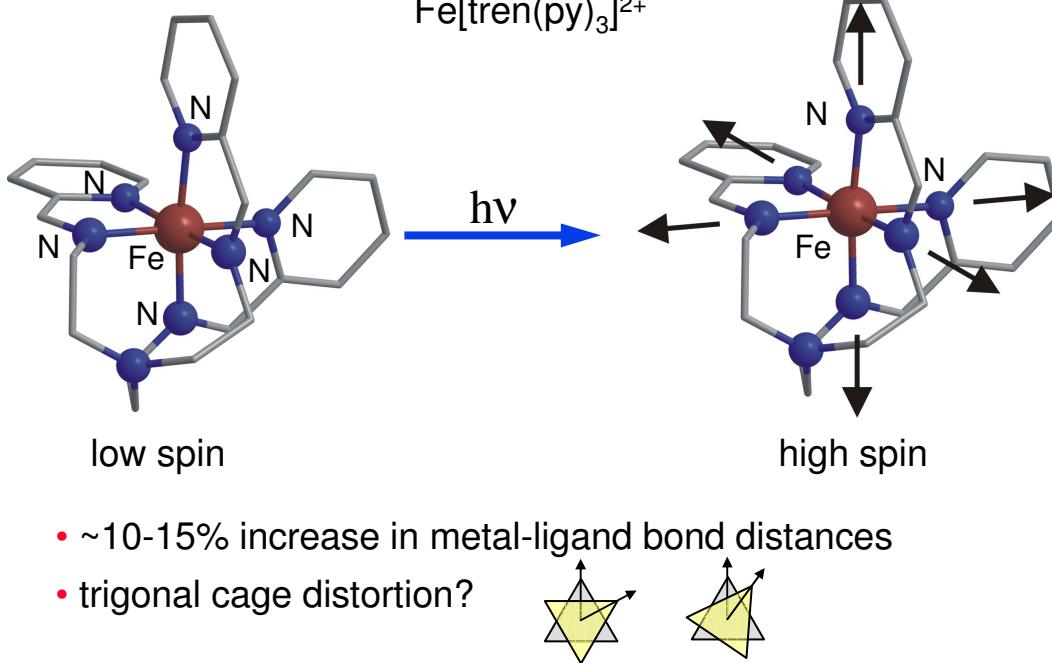
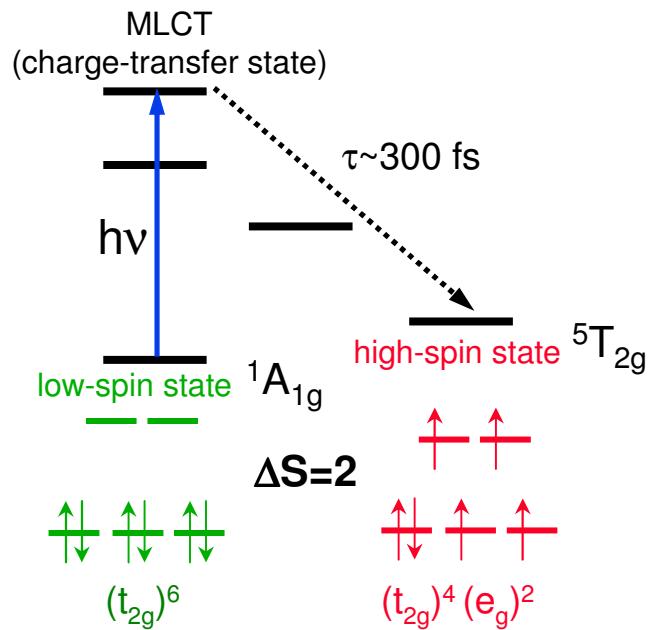
M. Rini, Y. Zhu, R. Schoenlein – LBNL Materials Sciences
S. Wall, R. Tobey, A. Cavalleri - Oxford



- Mn-3d/O-2p hybridization
- Modification of 10dq crystal field splitting



Fe^{II} Spin-Crossover Molecules



Motivation:

- ligand field strength ($10Dq$) ~ electron pairing energy
- relationship between structure, electronic, and magnetic properties

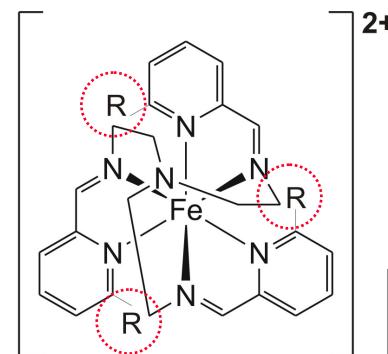
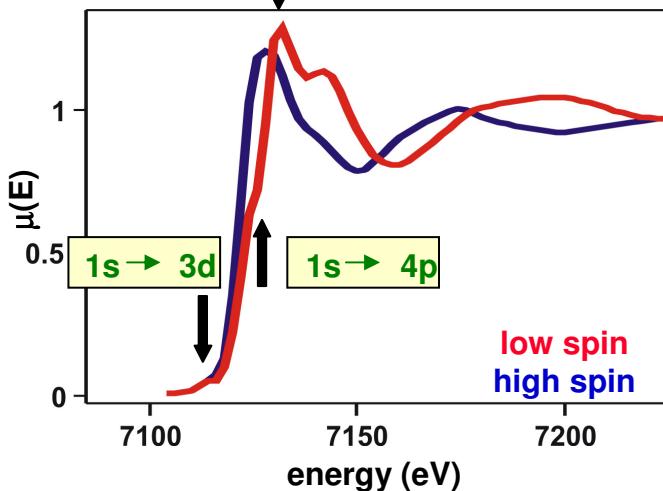
Do the dynamic structural distortions facilitate the spin-crossover reaction?

- electron transfer mechanistic role in biochemical processes (cytochrome P450)
- molecular electronics, opto-magnetic storage material



Static X-ray Absorption Spectra - Fe^{II} in Acetonitrile

(M. Khalil, M. Marcus – ALS BL 10.3.2)



chemically stabilized - synthesis:
A. Smeigh, J. McCusker

R=H (low spin)
Fe[tren(py)₃](PF₆)₂

R=CH₃ (high spin)
Fe[tren(6-Mepy)₃](PF₆)₂

Fe-N (Å)

Low spin

1.94 ± 0.01

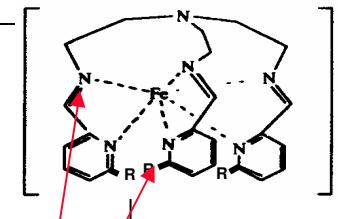
1.95

High spin

2.19 ± 0.01

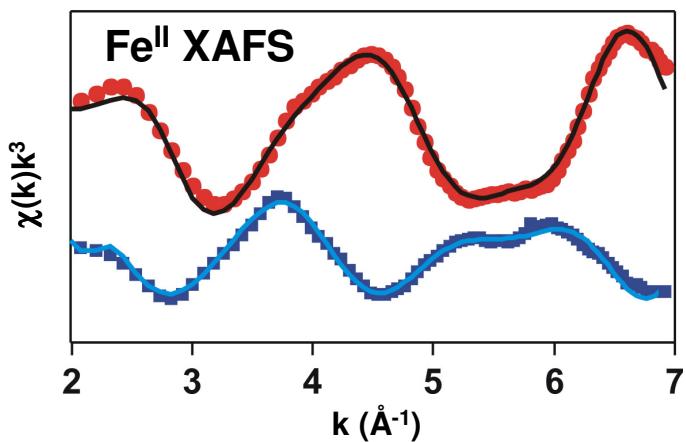
2.14 Fe-N (imine)

2.28 Fe-N (pyridine)

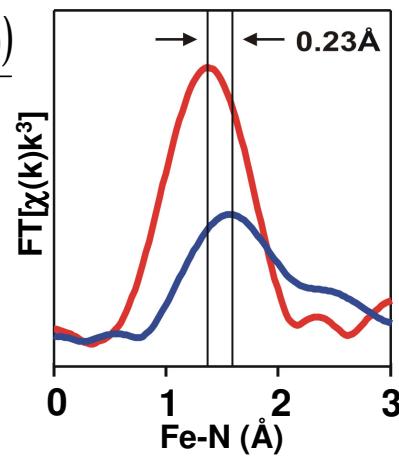


Fe 1s → 3d (distortion from octahedral symmetry)

Fe 1s → 4p (mixing of Fe-4s, -4p and N-2p)



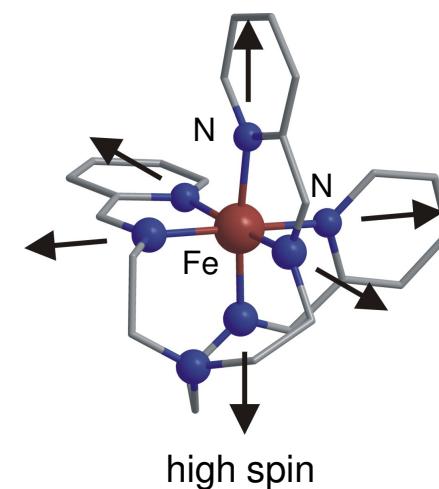
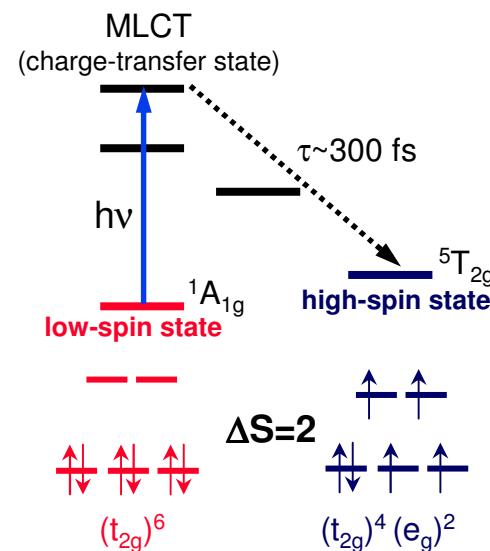
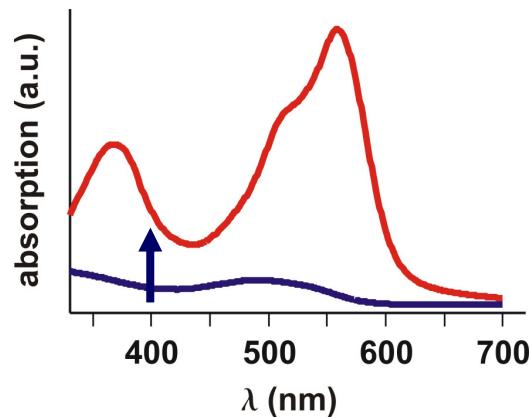
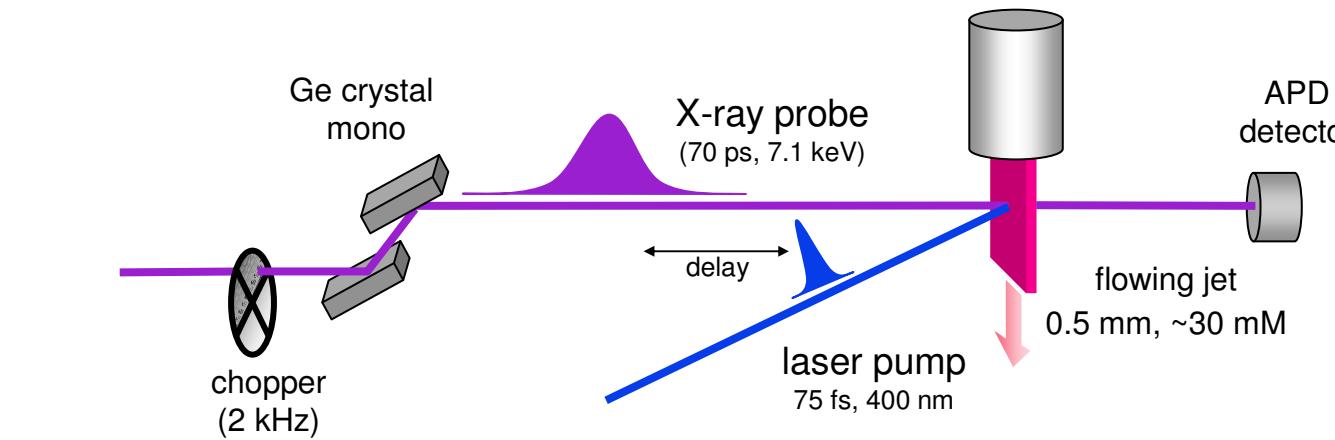
$$\chi(k)k^3 \sim \frac{\sin(2kr_j + \phi_{ij}(k))}{kr_j^2}$$



Time-resolved X-ray Absorption Spectra - Fe^{II} in Acetonitrile

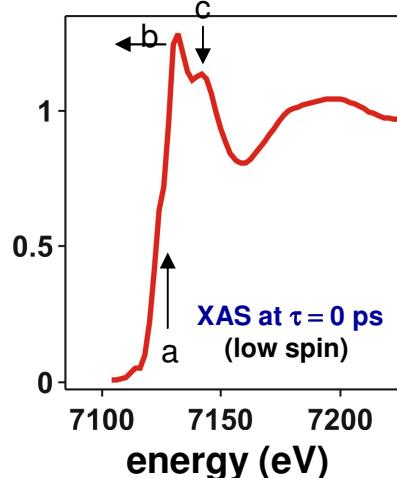
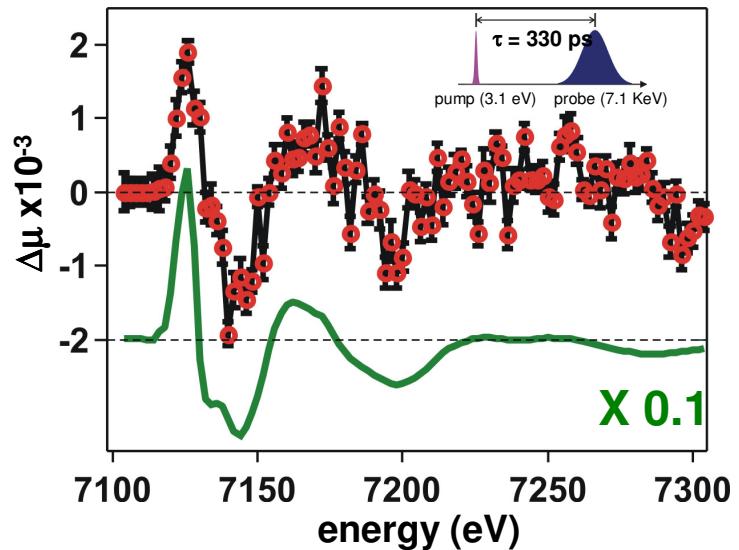


Time-resolved Spectra (ALS BL 5.3.1)

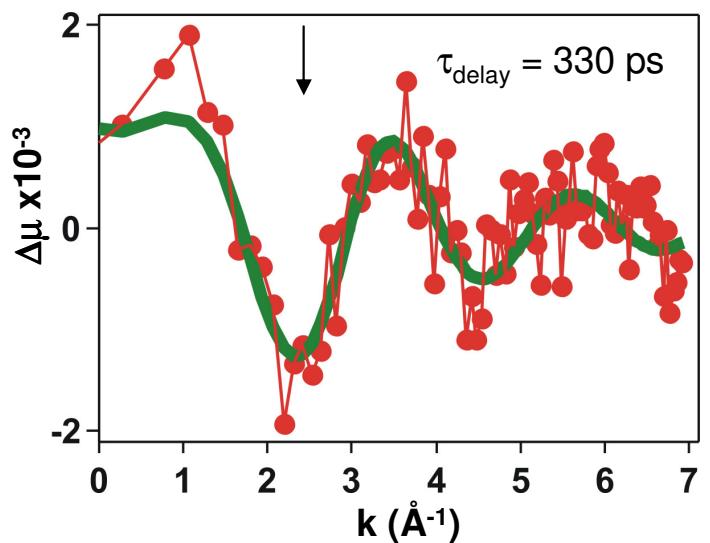




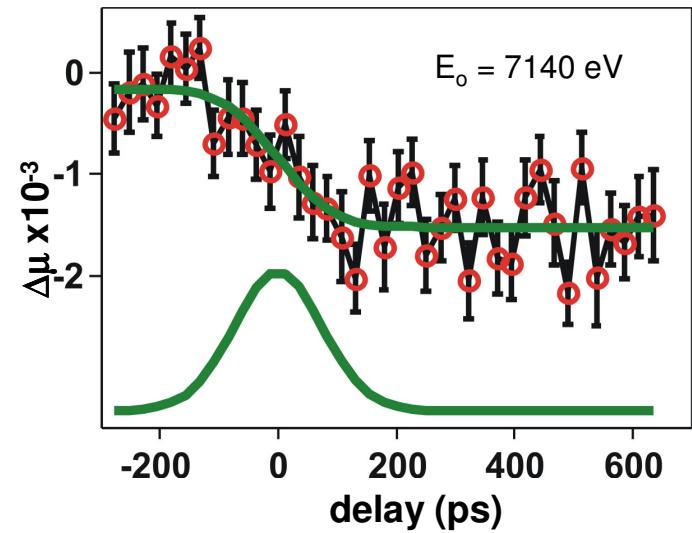
Fe^{II} Time-resolved EXAFS



Future: Femtosecond XAS
EXAFS: ligand structural dynamics
XANES: Fe oxidation state dynamics
Fe-N bonding
(Fe-4s,4p N-2p)



	Reactant	Photoexcited
$^1\text{A}_1 (\tau = 0)$	6 ± 0.5	6.5 ± 1
$R (\text{\AA})$	1.94 ± 0.01	2.15 ± 0.03
$\sigma (\text{\AA}^2)$	0.001	0.009



Fe^{II} Spin-Crossover Molecules - Future Directions



Soft X-ray XANES

Charge Transfer \Rightarrow Ligand Bonding \Rightarrow Spin State

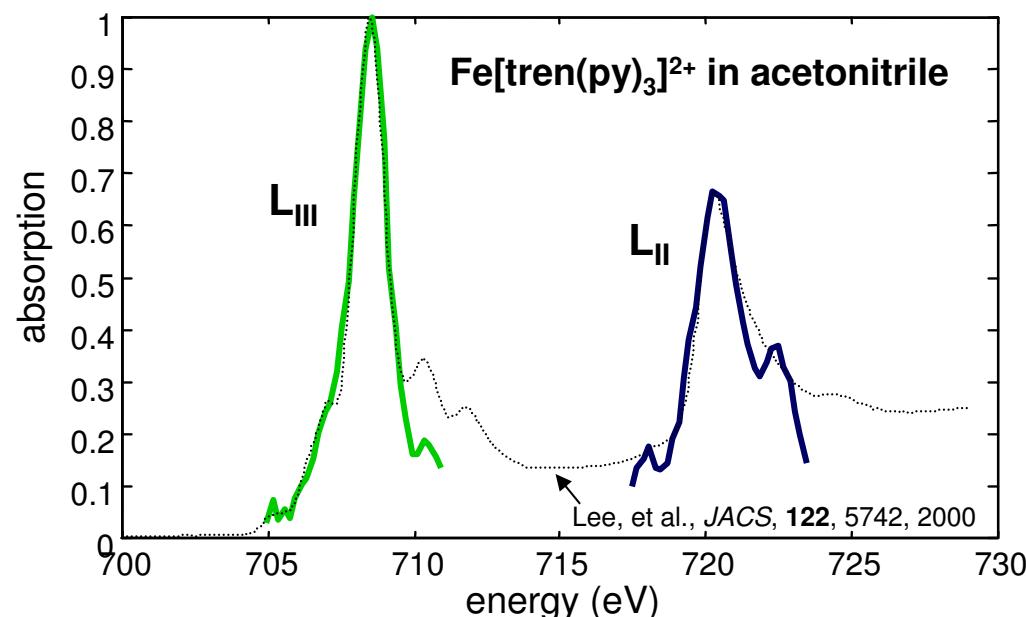
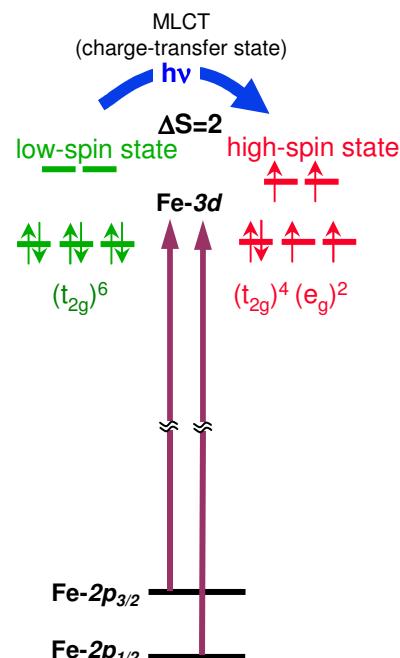
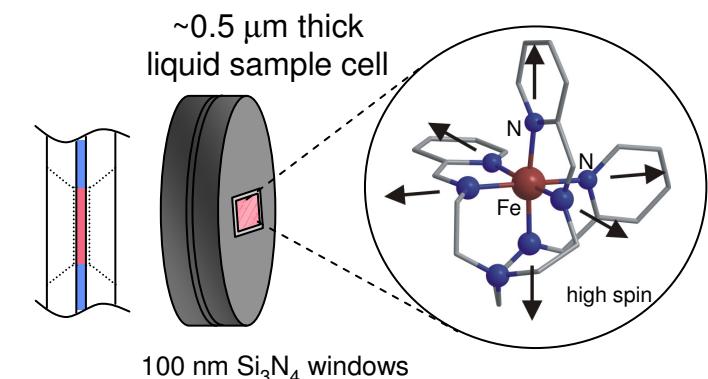
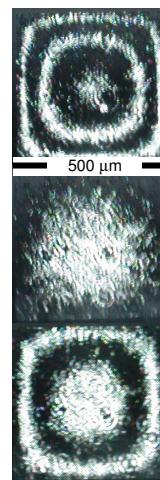
Electronic structure: L-edge spectroscopy

Metal-ligand bonding (high-spin vs. low spin)

- Fe 3d-electrons (N-2p)
- spin state (S-O split Fe-2p)

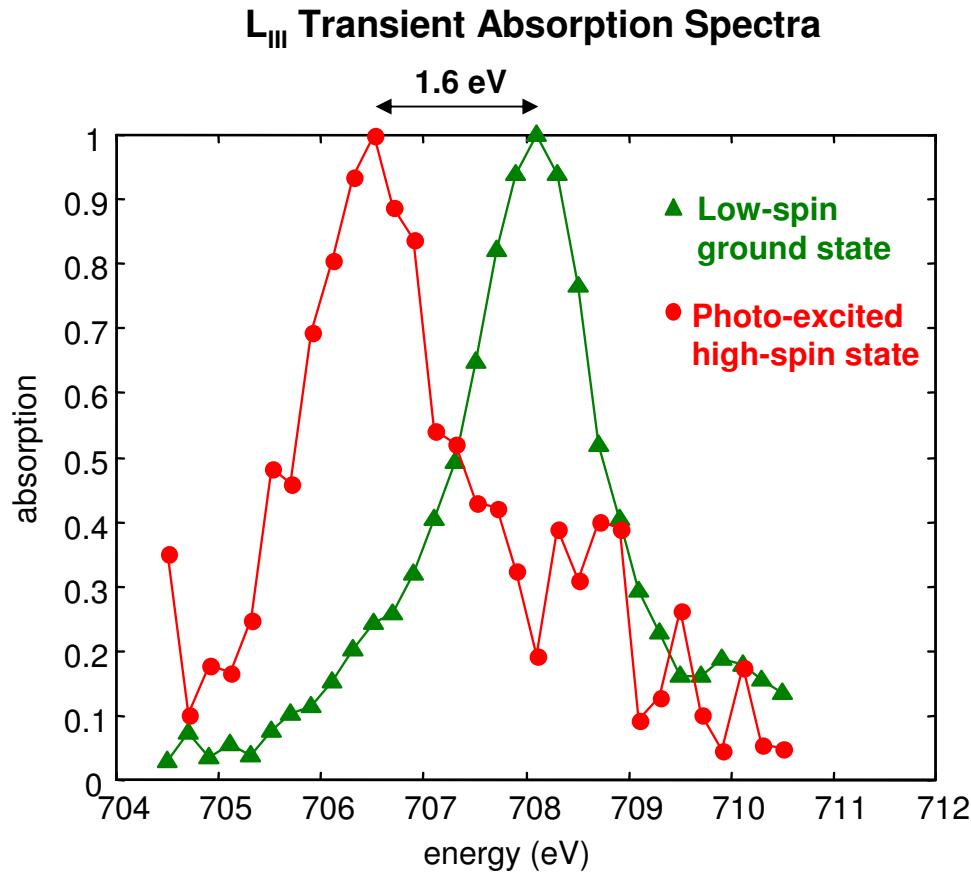
Solvent influence

- dielectric interaction with charge-transfer process
- steric interaction with ligand distortions?





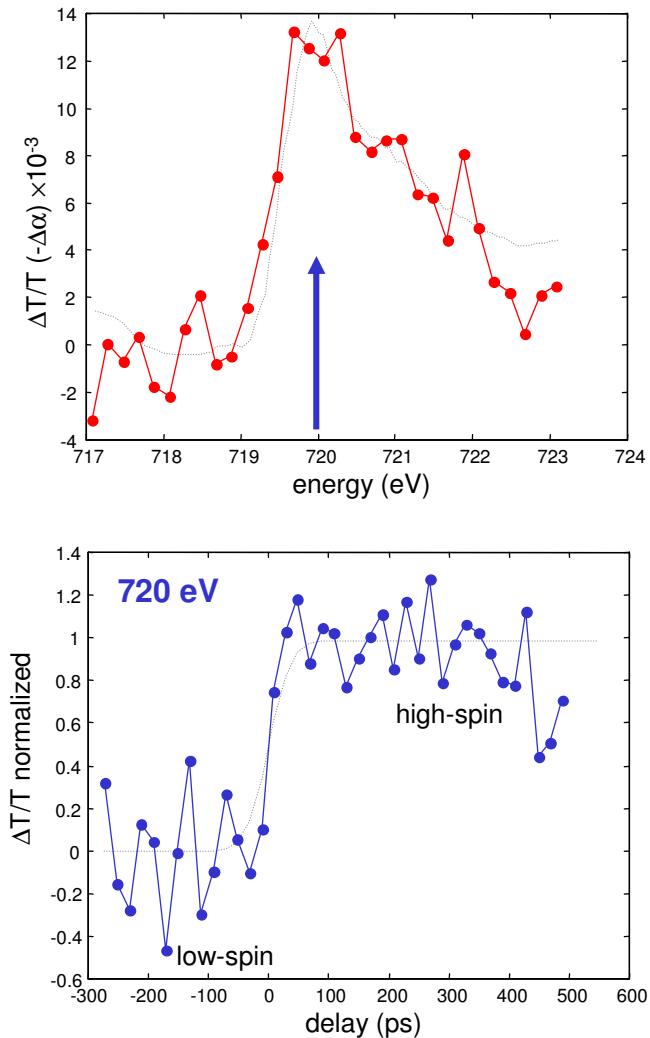
Future Directions - Fe^{II} Spin-Crossover L-edge XANES



Theory: (Brois et al., JACS, 117, 1995)

- ~0.55 eV reduction in 10Dq
- contribution from core-hole correlations

L_{II} Transient Absorption Spectra





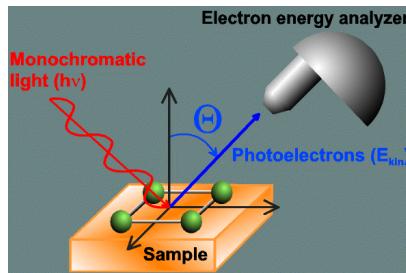
Dynamic Probe of Electronic Structure - Time-resolved ARPES

(Angle-Resolved Photoemission Spectroscopy)

Photoemission (ARPES) – $A(k,\omega)$ single particle spectral density function

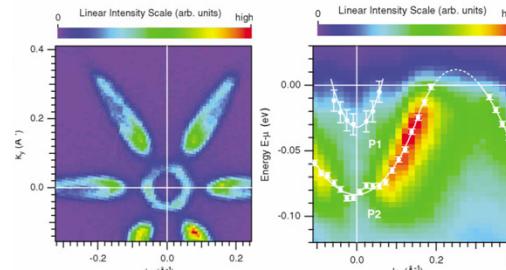
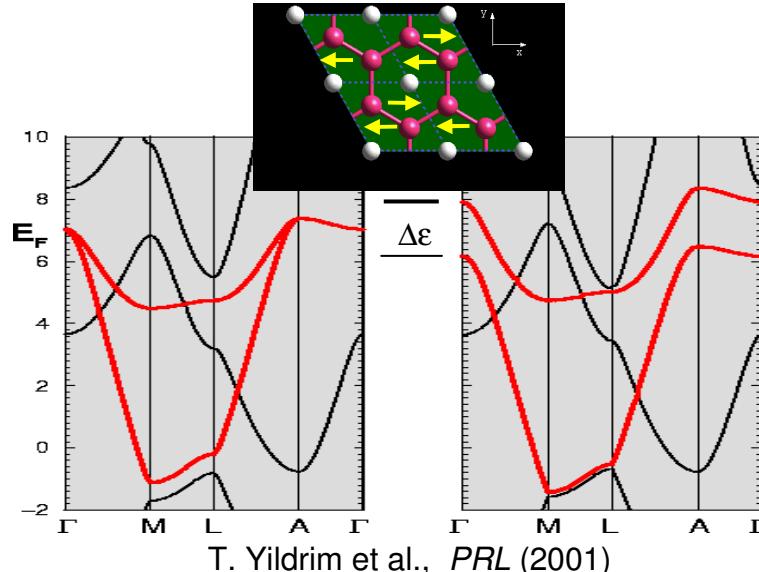
In response to tailored perturbation (vibrational/electronic, relevant energy scale)

Time-resolved – separation of correlated phenomena in time



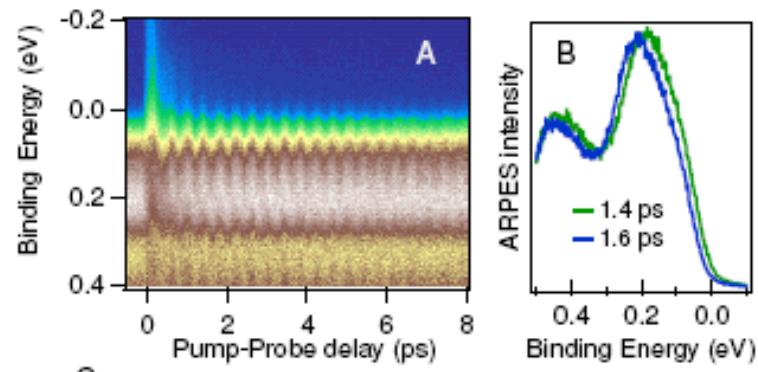
MgB₂ - Modulation of Electronic Structure

E_{2g} Mode (17 THz)



Bi - occupied electronic density of states

1T-TaS₂ - Modulation of Hubbard Gap coherent phonon excitation



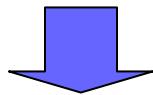
Perfetti, et al. PRL, 97, 067402 (2006)

Pseudogap/Cooper Pair Formation in Unconventional Superconductors

R. Kaindl

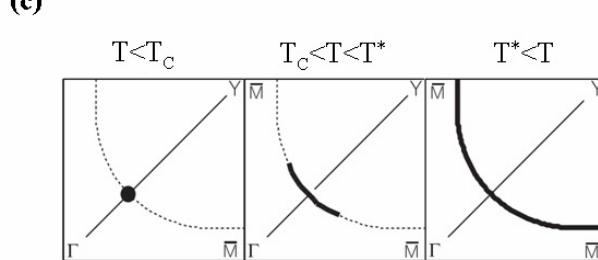
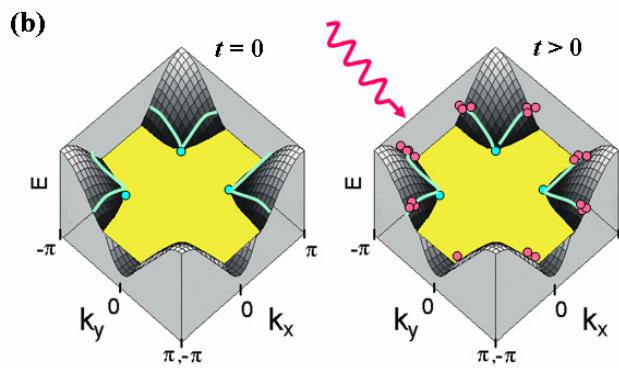
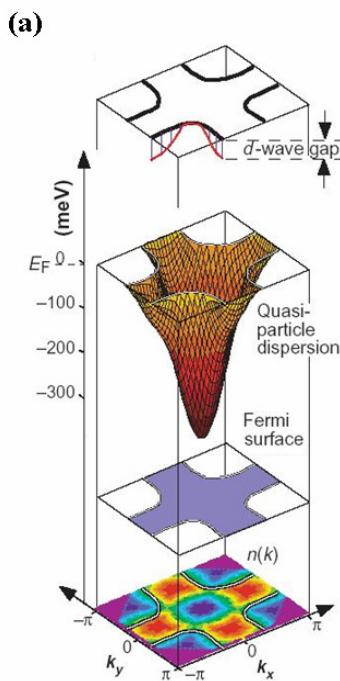
- in k -space, at relevant time scales (time-resolved ARPES, RIXS)
- in response to tailored perturbation - energy scale of $\Delta(k)$

Intense mid-IR femtosecond pulses



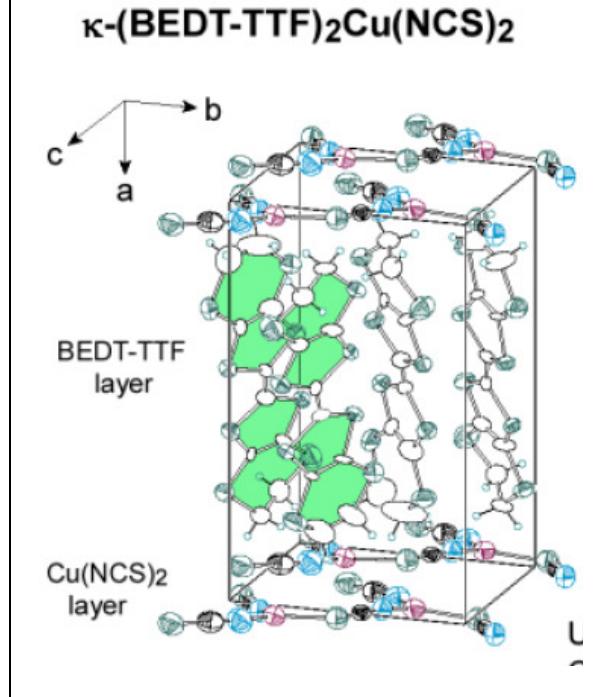
Non-thermal quasiparticle populations

Excited state $\Delta A(k,\omega)$: electronic couplings?
Formation kinetics of correlations (CPs, Gap)?
Separate electronic components in time?



Ronning et al., *Science* (1998)

application to organic systems



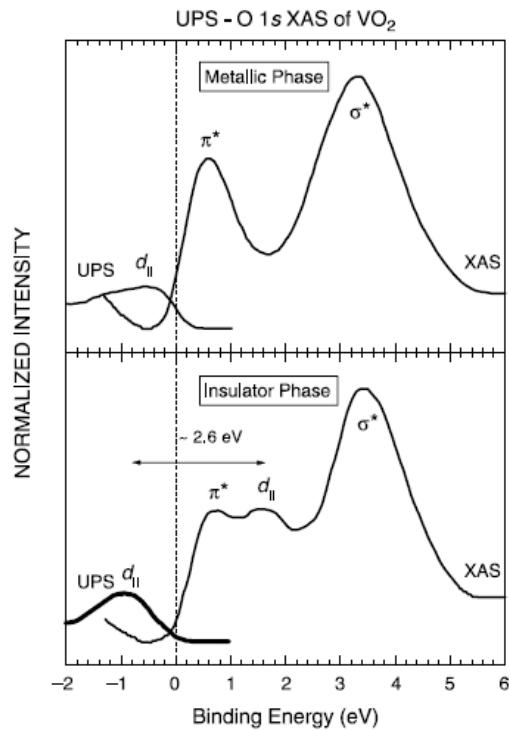
Direct (static) Probes of Electronic Structure

Soft X-ray Absorption – unoccupied energy states

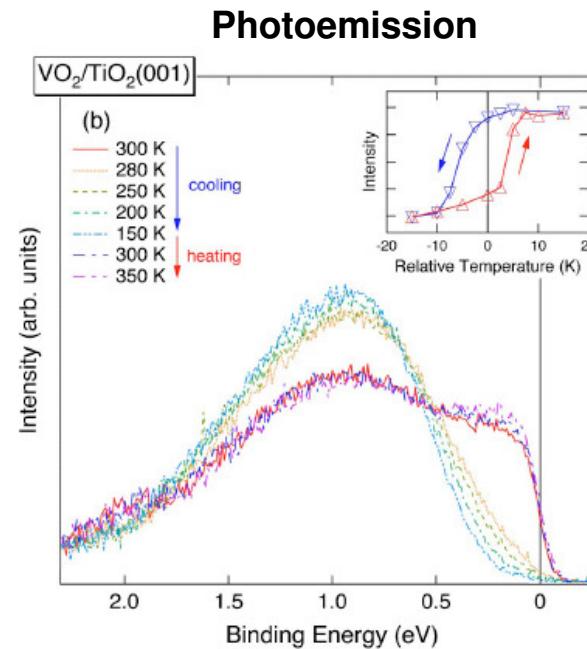
Photoemission (ARPES) – $A(k,\omega)$ single particle spectral density function

Time-resolved – separation of correlated phenomena in time

Soft X-ray Absorption



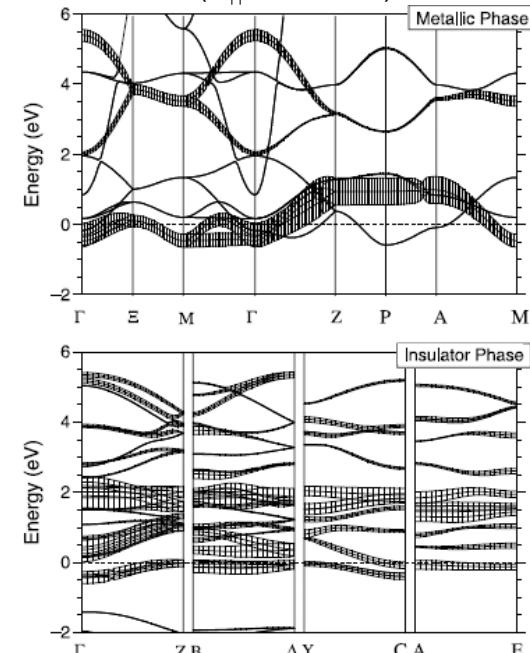
VO_2 M-I Transition (static)



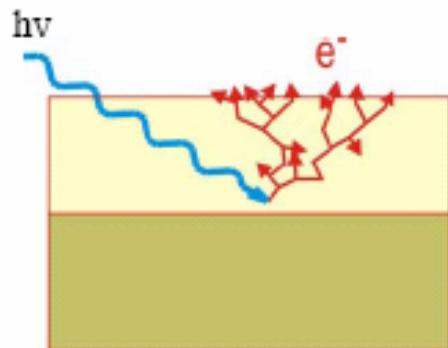
K. Okazaki et al., *PRB* **69**, 165104 (2004)

Abatte et al., *Sol. State Com.* **135**, 189 (2005)

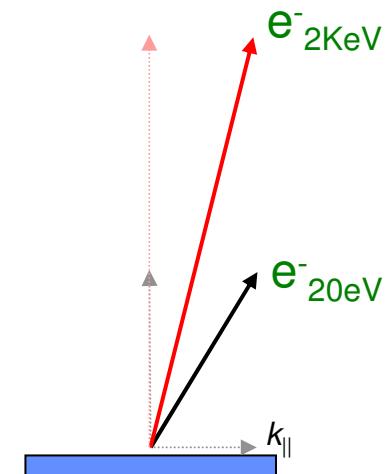
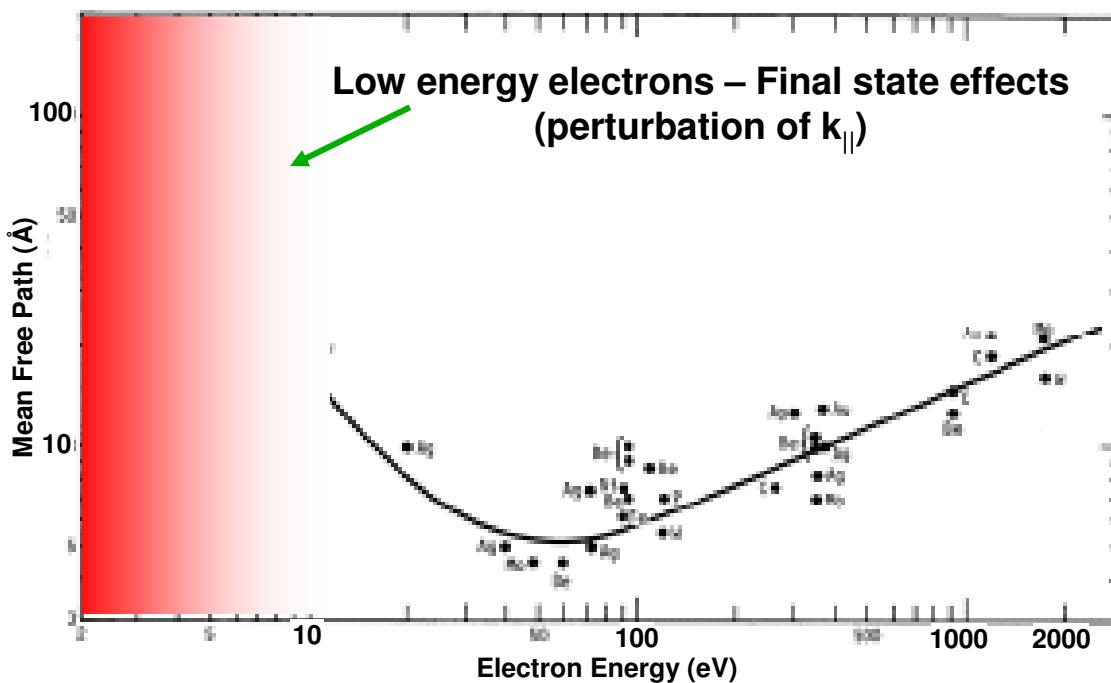
Theory: VO_2 Band Structure (d_{\parallel} character)



Time-resolved ARPES at KeV Energies



Electrons interact strongly
Surface Sensitivity
 $5\text{-}20 \text{ \AA}$

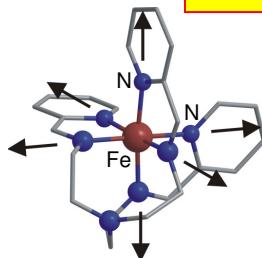


- KeV energy (10-100 meV res.)
- bulk penetration (VUV sources)
- Space charge distortion of EDC
low flux/pulse \Leftrightarrow high rep. rate
- Electron dynamics
rapid recovery \Leftrightarrow high rep. rate

Summary



Atomic and Electronic Structural Dynamics in Condensed Matter



- Structural Dynamics in Colossal Magnetoresistive (CMR) Manganites
- Structural Dynamics in Solvated Transition-Metal Complexes

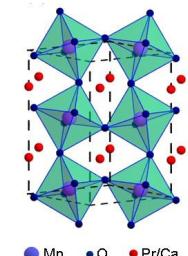
Scientific Challenges

Complex Correlated Materials

Strongly correlated systems
(high- T_c cuprates, CMR manganites)
Magnetic materials
(ferromagnetics, heterostructures)
Multiferroics
(ferromagnetism/ferroelectricity, interfaces)
Organics – molecular crystals

Molecular Dynamics – condensed phase

Solute dynamics
Solvent dynamics
Surface chemistry/catalysis



Light Source Capabilities

Ultrafast X-ray Spectroscopy
(XANES, XMCD, XMLD, EXAFS)
High Average Flux/Brightness
Synchronization
Tunability (300 eV – 10 KeV)
Soft x-rays – electronic structure
Hard x-rays – local atomic structure
Polarization Control
High Repetition Rate
Time and Angle Resolved Photoemission

Acknowledgements



M. Rini (PCMO)
Y. Zhu (PCMO)

LBNL - Materials Sciences Division

N. Huse - Fe(II)
M. Khalil* - Fe(II)

LBNL - Chemical Sciences Division - UXSL

*U. Washington

P.A. Heimann
T.E. Glover
M. Hertlein

LBNL - Advanced Light Source

A.L. Smeigh
J.L. McCusker
Michigan State University

S. Wall
A. Cavalleri
Oxford University